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Renewal time and transport of unventilated Central Intermediate Water of the Weddell Sea derived from biogeochemical properties

**Mario Hoppema^{1,3}, Hein J.W. de Baar², Eberhard Fahrbach³,
Richard G. J. Bellerby⁴**

ABSTRACT

We have investigated the intermediate water mass of the central Weddell Gyre using TCO_2 and oxygen data of FS *Polarstern* cruises in 1992, 1996 and 1998. This water mass, designated as Central Intermediate Water (CIW), is enriched in CO_2 and depleted in O_2 relative to its source water due to biological degradation. CO_2 enrichment and O_2 depletion were quantified by calculating the difference between the concentrations in the CIW and those in the more southern source water, the Circumpolar Deep Water, which derives from the Antarctic Circumpolar Current. Inventories of enrichment and depletion were determined over the whole depth range of CIW, i.e. about 200–800 m. The O_2 depletion inventory was greater than that of TCO_2 enrichment which is in line with a biological origin of the signal. Spatial and interannual variation appeared to be small. Because subsurface remineralization in the central Weddell Gyre is largely restricted to the CIW, the export production estimate from previous work has been applied to compute the renewal time of CIW from these inventories. A renewal time of only three years was found. TCO_2 - and O_2 -based computations were consistent, the former showing larger variation, though. From renewal time and volume of the CIW, a transport velocity (renewal rate) of 6–7 Sv was obtained. Of this, about 1 Sv is upwelled into the surface layer. The remaining 5–6 Sv CIW must be exported to the north, which is opposite to previous views. Results of water mass age and transport rate have thus been obtained using a method based on biogeochemical parameters. As the CIW cannot be identified by temperature and salinity, nor with transient tracers because it is hardly ventilated, this is the only way to obtain such results. As part of the CIW export, a large amount of remineralized CO_2 enters the abyssal oceans where it is sequestered for long periods of time. The CIW is a principal and highly efficient player in the biological pump mechanism of the Southern Ocean.

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1. Introduction

The bottom layers of the world oceans are largely replenished by high-density waters from the high latitudes. Dense water deriving from the south is commonly designated as Antarctic Bottom Water (AABW). The Weddell Sea in the Atlantic sector of the Southern Ocean has long been considered to be the prevailing source region of dense waters within the Southern Ocean (Brennecke, 1921; Deacon, 1933; Carmack, 1977). Recently, this appeared to be confirmed by a comprehensive analysis based on chlorofluorocarbon (CFC) budgets by Orsi *et al.* (1999). The Atlantic sector was reported to contribute 60% of the total AABW production of the Southern Ocean. However, other recent studies suggest that the role of the Weddell Sea may have been overestimated (Meredith *et al.*, 2000; Hoppema *et al.*, 2001). AABW sources to the east and off Adélie Land were found to be highly significant (Rintoul, 1998). In fact, these results and those by Orsi *et al.* (1999) are not inconsistent. Orsi *et al.* (1999) defined the Atlantic sector quite generously toward the east between 70W and 80E, thus including a large region outside the Weddell Sea proper. The studies by Meredith *et al.* (2000) and Hoppema *et al.* (2001) suggest that a sizable part of the AABW production occurs east of the Weddell Sea but within the wider sector as defined by Orsi *et al.* (1999).

In addition to AABW, another water mass fills the bottom layers of the basins north of the Southern Ocean, namely the water from the lower part of the Circumpolar Deep Water (Mantyla and Reid, 1983; Orsi *et al.*, 1999). The latter authors designate this as Antarctic Circumpolar Current bottom water (ACCBw). In the Atlantic sector this water mass is a mixing product of the North Atlantic Deep Water above and the AABW below. Additionally, it is replenished laterally from the south, i.e. the subpolar regime, by modified Circumpolar Deep Water (CDW) of the same density (Orsi *et al.*, 1999).

Here we draw attention to a modification of CDW occurring in the central part of the Weddell Gyre which has previously been described by Whitworth and Nowlin (1987) and denoted Central Intermediate Water (CIW). These authors, and later also Orsi *et al.* (1993), consider CIW to be that portion of the CDW that is too dense to mix with shelf waters along the margins of the Antarctic continent. They propose that it recirculates within the gyre and is ultimately eroded away from above. However, this suggestion is only a qualitative assessment and there is little evidence to support it. This modified form of CDW could instead feed back to the ACCbw. The importance of the CIW lies in the fact that it is enriched in nutrients and CO₂ (Whitworth and Nowlin, 1987; Hoppema *et al.*, 1997). CIW cannot be identified by its potential temperature-salinity field, but only discerned in the data fields of nutrients, TCO₂ or oxygen (Whitworth and Nowlin, 1987). It is worthwhile exploring the properties of the CIW both with respect to its significance as a water mass and to its role in the biological pump of the Weddell Gyre. We quantify the enrichment of CO₂ and the reduction of O₂ in the CIW. This is done for different regions of the central Weddell Gyre using data of different years, which should account for possible effects of spatial and interannual variability. With the spatial extent of the CIW, the total inventories of biologically generated subsurface CO₂ and O₂ depletion of the central Weddell Gyre are

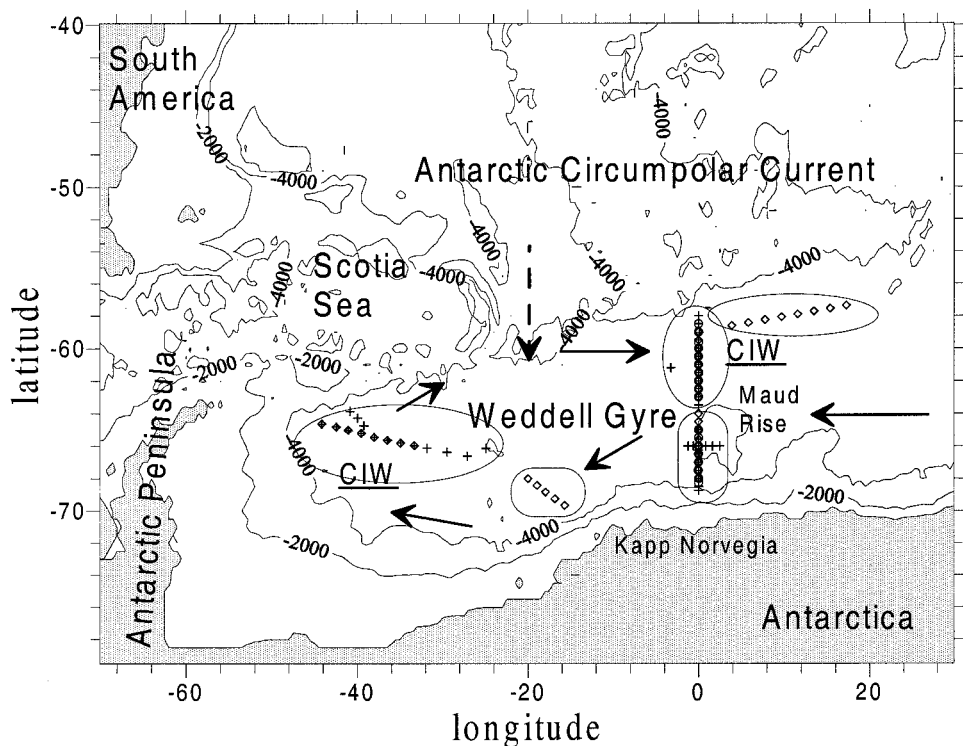


Figure 1. Map of the study area featuring station positions; circles (only along prime meridian) for cruise ANT X/4 (1992), diamonds for ANT XIII/4 (1996) and crosses for ANT XV/4 (1998). Subregions of southern Weddell Gyre stations and CIW stations are indicated. Arrow shows the main water flow direction in the southern gyre.

determined. Because subsurface remineralization in the Weddell Gyre is essentially restricted to the CIW, an earlier independent estimate of export flux (Hoppema *et al.*, 1999) provides the additional constraint as required to resolve the renewal time of CIW from the remineralization rate.

2. Methods and data

Data are presented from three cruises in the Weddell Sea and environs, ANT X/4 in June/July 1992 (Lemke, 1994), ANT XIII/4 in April/May 1996 (Fahrbach and Gerdes, 1997) and ANT XV/4 in April/May 1998 (Fahrbach, 1999) with the German ice breaker FS *Polarstern*. We use data of transects across the Weddell Gyre, one at the prime meridian and one in the western Weddell Sea and additionally, one along the eastern part of the gyre (Fig. 1). Here we show data of total carbon dioxide (TCO_2) and dissolved oxygen (O_2). Data from cruises ANT X/4 (1992) and ANT XIII/4 (1996) have also been presented

elsewhere (Hoppema *et al.*, 1997; 1999; 2000) in which, however, different issues were treated.

Water samples were collected all through the water column with a General Oceanics rosette sampler which was coupled to a Conductivity Temperature Depth (CTD) instrument. The samples were more closely spaced in the upper 1000 m. Temperature and salinity data were derived from the CTD. The accuracy of the former was set by shore-based calibration and is better than 3 mK and that of the latter is 0.003 (Practical Salinity Scale). Dissolved oxygen was measured with a standard automated Winkler technique with photometric end-point detection, precision 0.2%.

TCO₂ was determined with the coulometric method after Johnson *et al.* (1987) as slightly modified by Robinson and Williams (1992) and Stoll (1994). The TCO₂ concentration is the sum of all carbonate species dissolved in seawater, i.e. $\text{TCO}_2 = [\text{CO}_2] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$. For the prime meridian data of cruise ANT XIII/4, 68 duplicates were measured which on average differed by $1.4 \mu\text{mol kg}^{-1}$. For the Weddell Sea part of the cruise this difference is $1.0 \mu\text{mol kg}^{-1}$. For cruise ANT XV/4 the precision is $1.5 \mu\text{mol kg}^{-1}$ (0.065%), as obtained from 21 duplicates, all samples being taken at one depth. Accuracy on cruises ANT XIII/4 (1996) and ANT XV/4 (1998) was set by certified reference material (DOE, 1994) made available by Prof. A. Dickson of the Scripps Institution of Oceanography (USA). Standards were measured for each cell prepared for the coulometer and the cells were changed about once a day. Data collected during the utilization of one cell were corrected using the standard measured for this cell.

3. Computational aspects

Diagrams of TCO₂ and O₂ against potential temperature (θ) at the prime meridian in 1998 are displayed to highlight the properties of the Central Intermediate Water (Fig. 2). The properties are similar in the other years (not displayed here). Data were subdivided according to their respective hydrographic regime. The southern Weddell Gyre represents the least modified Circumpolar Deep Water from the Antarctic Circumpolar Current (ACC) at this longitude (Whitworth *et al.*, 1998; Schröder and Fahrbach, 1999). It is characterized by a high temperature maximum ($0.8\text{--}1.3^\circ\text{C}$), which was referred to as warm regime water by Gordon and Huber (1990). In the central Weddell Gyre the temperature maximum is much reduced because of interactions with shelf and slope waters (Orsi *et al.*, 1999), with the upstream topographic high Maud Rise (Gordon and Huber, 1990; Muench *et al.*, 2001), and mixing with waters above and below (Whitworth *et al.*, 1998). The central Weddell Gyre (57.5S to 62.5S) was called cold regime water by Gordon and Huber (1990). The CIW is part of the cold regime. It is evident from Figure 2 that in the CIW ($\theta > 0^\circ\text{C}$), TCO₂ is higher and O₂ lower than at the corresponding temperatures in the southern, more pristine Weddell Gyre. As demonstrated by Whitworth and Nowlin (1987), this can only be caused by degradation of organic material in the subsurface waters. It is important to note that there is only a difference between the central and southern Weddell Gyre at temperatures higher than 0°C . In the underlying Weddell Sea Deep Water ($-0.7^\circ\text{C} < \theta <$

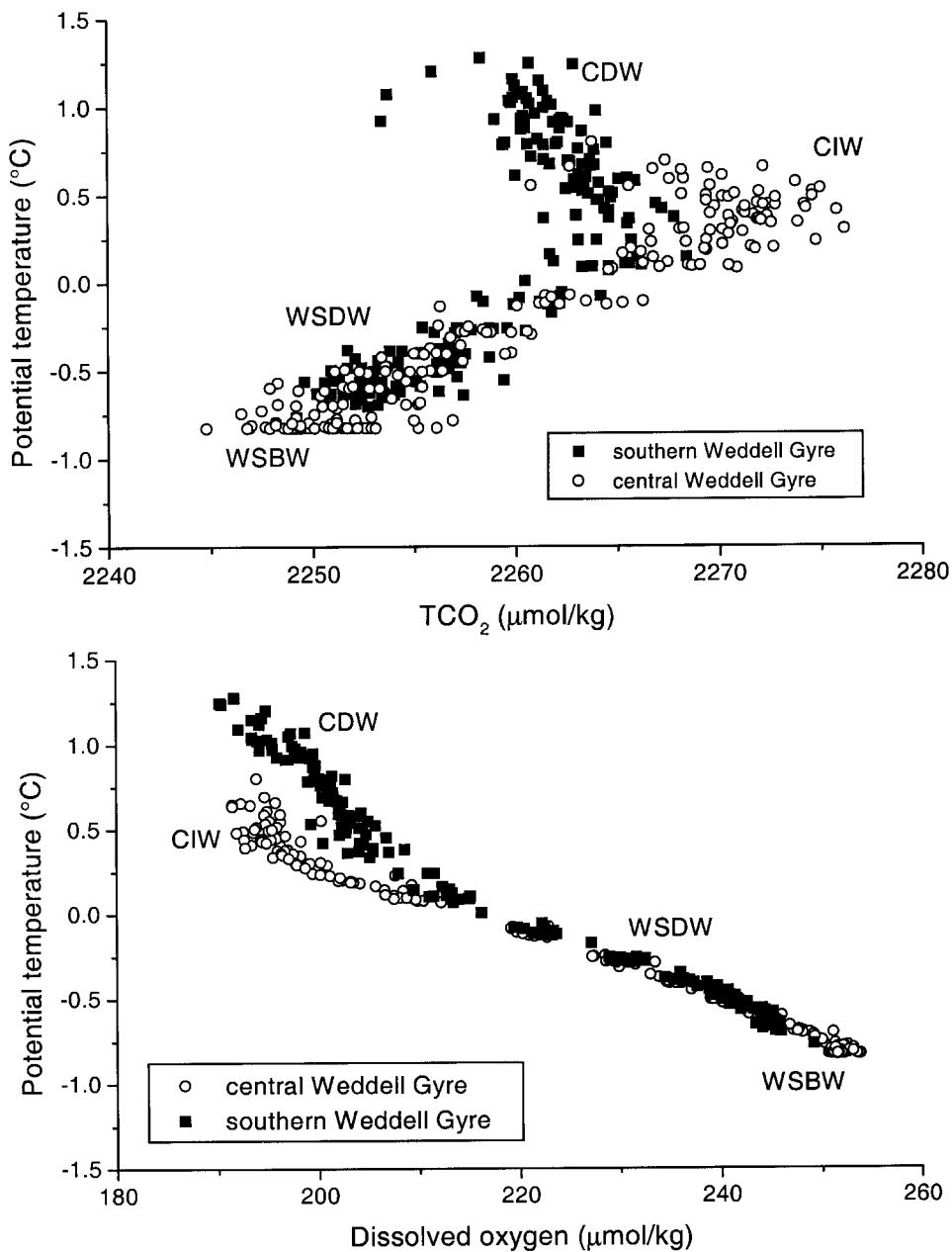


Figure 2. Scatter plots of TCO₂ and oxygen against potential temperature for data of cruise ANT XV/4 (1998) at the prime meridian. Only data from below the temperature maximum are shown. Data of the southern and central Weddell Gyre have different symbols to highlight the Central Intermediate Water. CDW Circumpolar Deep Water; CIW Central Intermediate Water; WSDW Weddell Sea Deep Water; WSBW Weddell Sea Bottom Water.

0°C), TCO_2 and O_2 are indistinguishable in the two regimes, which indicates that in the deep Weddell Gyre remineralization activity is negligibly small on the time scale of recirculation of deep water. This observation is in line with the notion that remineralization in the Weddell Gyre is almost completely restricted to the upper few hundred meters of the water column (Usbeck *et al.*, 2002). Only a minor part of organic matter is exported to the abyssal Weddell basin (Hoppema *et al.*, 1998).

We use the differences between the southern and central gyre to compute the net enrichment of TCO_2 and the depletion of O_2 in the CIW. On its way through the Weddell-Enderby basin, this southern CDW shoals and is enriched in CO_2 and reduced in O_2 *en route*. Finally then it is termed Central Intermediate Water. This is the modification that occurs during the transit of CDW from the southern part of the gyre at the prime meridian to the central part of the gyre at the prime meridian. We do not know exactly the flow path of this CDW. Also note that this is not the entire enrichment/reduction of the CIW, because some may have occurred east of the prime meridian section where CDW of the ACC enters the Weddell Gyre (Bagriantsev *et al.*, 1989; Gouretski and Danilov, 1993).

In determining the difference between the central and southern gyre (see Fig. 2), we must account for the temperature range within the southern source water and the CIW. During its course through the gyre, the warmest CDW from the southern gyre (see Fig. 2) is eroded away by mixing with surface water. The deeper fraction of southern CDW with lower temperature, then, is the direct source water for the CIW. We selected all warm regime stations from the southern gyre. This includes stations north and south of Maud Rise, but excludes the coastal current. Most westward flow occurs north of Maud Rise (Schröder and Fahrbach, 1999; Muench *et al.*, 2001), but also some part takes the southern route. Thus, first the relationships of TCO_2/O_2 and potential temperature for the southern part of the gyre at the prime meridian were determined for all cruises separately. Only data from below the temperature maximum were included. Data points that are obviously affected by mixing with surface water with low salinity and temperature were discarded. The remaining points of the CDW in the θ -S diagram form essentially a linear relationship. The TCO_2 and O_2 data corresponding to the θ -S data that deviate from the linear relationship were not included in the analysis. Regression results of potential temperature versus TCO_2 and O_2 relationships for the southern Weddell Gyre at the prime meridian appear in Table 1. These relationships can be considered as describing the source water which is to be modified to CIW. It is evident that the relationships display interannual variability, where the 1998 data are generally higher both for TCO_2 and O_2 . Interannual variations in the CDW have been observed before (Gordon, 1982; Fahrbach, 1999), and it is clear that the temperature maximum in recent years is significantly higher than in earlier years (compare Whitworth and Nowlin, 1987; Gordon and Huber, 1990; Schröder and Fahrbach, 1999). This may be caused by interannual variability of the inflowing CDW.

As a next step of the analysis, the stations with CIW characteristics were selected. We took the stations with an O_2 minimum and TCO_2 maximum shallower than 400 m. Those are stations associated with the axis region of the Weddell Gyre, i.e. where the isopycnals

Table 1. Values of the coefficients of the relationship $\text{TCO}_2 = A \times \text{potential temperature} + B$ and oxygen = $A \times \text{potential temperature} + B$ for the southern limb of the Weddell Gyre at the prime meridian for three different cruises.

	ANT X/4 1992	ANT XIII/4 1996		ANT XV/4 1998	
	oxygen	oxygen	TCO_2	oxygen	TCO_2
A	−13.465	−12.442	−8.576	−13.962	−7.278
B	212.31	206.70	2265.4	211.16	2268.1
Regression coefficient	−0.888	−0.903	−0.813	−0.932	−0.824
Standard deviation	1.424	1.377	1.456	1.277	1.095
Number of data points	42	40	34	77	61

of the CIW reach the shallowest depth (Whitworth and Nowlin, 1987; Fahrbach *et al.*, 1994). Obviously, these are exactly the stations that have an oxygen minimum that is much lower and TCO_2 maximum that is much higher than those in the adjacent southern gyre. The regions with CIW characteristics for the different cruises appear in Table 2. There is variability of the locations between the years, especially where 1998 deviates. The position of the CIW regions complies approximately with that beyond the warm regime in Schröder and Fahrbach (1999). The TCO_2 enrichment and O_2 reduction of the CIW were obtained by subtracting the “initial” values of the southern gyre from those at the CIW stations at the appropriate potential temperatures. For the CIW stations of a certain year we applied the “initial” relationships of that same year (Table 1). The upper boundary of the CIW occurred at 140–200 m depth, just below the permanent pycnocline, whereas the lower boundary was set at a potential temperature of 0°C, which is the lower boundary of CDW entering the Weddell Gyre from the ACC (Whitworth *et al.*, 1994). Note that Whitworth and Nowlin (1987) suggested a lower boundary of 0.2°C. Our analysis shows that 0°C is the appropriate boundary because at this temperature the TCO_2 enhancement and O_2 reduction indeed reach zero (see later).

Finally, the O_2 reduction and TCO_2 elevation within the CIW were computed by integrating over the whole depth range of the CIW. Integration was done per station from the top of the CIW just below the pycnocline to the bottom defined by potential temperature of 0°C. Stations were averaged to yield the inventory for a specific region

Table 2. Locations of the CIW regions during the different cruises.

Cruise year and subregion	Station numbers	Geographical coordinates
1992 prime meridian	580–590	58.5–63.5S
1996 prime meridian	42–51	59–63.5S
1998 prime meridian	100–113	57.5–63.5S
1996 west Weddell	87–95	33.3–45.8°W, 66–64.4S
1998 west Weddell	19–34	24.9–44.2°W, 66.1–64.6S
1996 east Weddell	22–30	1.9–17.3°E, 58.8–57.4S

Table 3. Inventories (with standard error due to station scatter) of oxygen depletion and TCO₂ enrichment of the Central Intermediate Water at different locations within the Weddell Gyre and for different years. Also the calculated mean renewal times of the CIW are given based on these different inventories. Errors in renewal time additionally include those of the measurement, of the linear fit of source water (see Table 1) and of the export production (Section 5a). n is the number of stations averaged.

	CIW oxygen depletion (mol m ⁻²)	n	Oxygen renewal time (years)	CIW TCO ₂ enrichment (mol m ⁻²)	n	TCO ₂ renewal time (years)
<i>prime meridian</i>						
1992	6.70 ± 0.28	10	2.6 ± 0.9	no data	—	—
1996	7.34 ± 0.33	10	2.8 ± 1.0	5.76 ± 0.70	9	3.2 ± 1.7
1998	6.01 ± 0.26	12	2.3 ± 0.9	3.78 ± 0.40	12	2.1 ± 1.2
<i>west Weddell</i>						
1996	8.07 ± 0.40	9	3.1 ± 1.1	6.58 ± 0.45	9	3.7 ± 1.7
1998	8.10 ± 0.19	15	3.1 ± 1.0	4.34 ± 0.37	14	2.4 ± 1.3
1996*	5.30 ± 0.46	9	2.0 ± 0.8	—	—	—
<i>east Weddell</i>						
1996	7.57 ± 0.18	9	2.9 ± 0.9	5.94 ± 0.39	9	3.3 ± 1.4

*In this case the relationship of oxygen versus potential temperature was taken from the western Weddell Sea off Kapp Norvegia.

and year. Results for different cruises (years) and regions of the Weddell Gyre appear in Table 3.

4. Results

A scatter plot of O₂ reduction and TCO₂ enrichment in the CIW is depicted in Figure 3 for the western Weddell Sea in 1996. Note that both the O₂ reduction and the TCO₂ enrichment are given as positive values in this plot. A fair correlation exists between TCO₂ enrichment and O₂ depletion. At intermediate values the scattering is enhanced. The correlation may be somewhat lowered because the remineralization horizons of CO₂ and O₂ are different, that is, nutrients are remineralized higher in the water column than CO₂ (e.g. Shaffer, 1996) while O₂ incorporates the effects of all remineralization.

The trend perceived in Figure 3 is in keeping with the magnitudes of the inventories (Table 3). Inventories of O₂ depletion are larger than those of TCO₂ enrichment. The CIW inventories for the western Weddell Sea tend to be higher than for the prime meridian and eastern Weddell Gyre. Interannual variability in O₂ depletion inventories is small. TCO₂ enrichment inventories in 1998 data are clearly lower than in 1996 both for the prime meridian and the western Weddell Sea. This is caused by the different “initial”

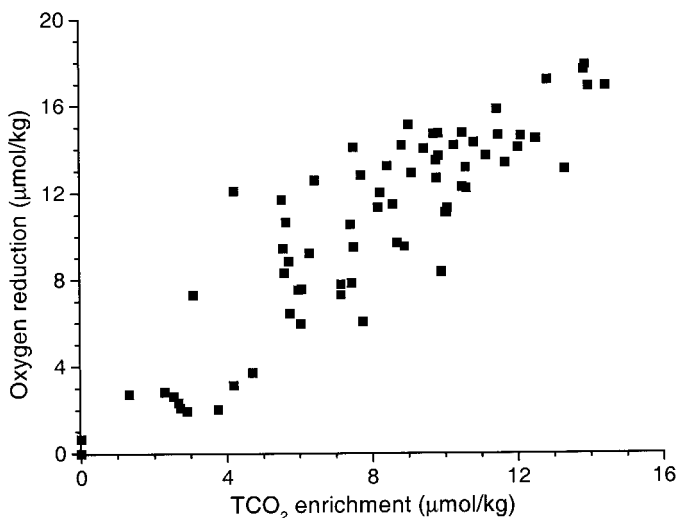


Figure 3. Scatter plot of TCO₂ enrichment versus oxygen reduction in CIW of the western Weddell Sea during cruise ANT XIII/4 (1996).

relationships (Table 1). Recall that the location of the CIW also changes from year to year (Table 2). For the O₂ depletion inventory, only the 1998 data at the prime meridian tend to be lower. Interannual variability of the CDW inflow may be the ultimate cause.

For the western Weddell Sea we also calculated an “initial” relationship of oxygen and potential temperature using data from the warm regime of the western Weddell Sea itself (i.e. off Kapp Norvegia, see Fig. 1, and not from the prime meridian like for all others). This should explore the possibility of an additional inflow of CDW into the western Weddell Sea near 20W (Bagrientsev *et al.*, 1989). Results appear in Table 3 under “west Weddell”; for this exercise only data from 1996 are available. Clearly, the O₂ depletion inventory thus obtained (5.30 mol m^{-2}) is smaller than when the assumed inflow occurs in the east (inventory: 8.07 mol m^{-2}). This issue is discussed in more detail below.

5. Discussion

a. CIW renewal time

Knowing the CIW inventory of O₂ reduction and TCO₂ enrichment, the renewal time of the CIW can be calculated. As mentioned, the reduction of O₂ and enrichment of TCO₂ in the subsurface CIW is caused by degradation of organic material that has been produced in the overlying surface layer. The property that describes the net loss of organic material from the surface layer is the export production, i.e. that part of the primary production that is exported from the surface layer. In the Weddell Gyre, significant degradation of organic matter occurs only in the CIW. With the inventory of TCO₂ enrichment, we possess the total amount of remineralized carbon present in the CIW and with the export production,

the annual supply of carbon to the CIW. Hence by dividing inventory by export production, the renewal time of the CIW is obtained. For O_2 reduction and its inventory the reasoning is similar.

Since the assumption that all export production is remineralized within the CIW depth range (<800 m) is so important, but not generally valid for the world oceans, we justify it here. Firstly, within the Weddell Sea the surface layer depletion of ^{234}Th (a fine tracer for export production) is balanced by a ^{234}Th enrichment in the subsurface (CIW) layer of equal magnitude (Usbeck *et al.*, 2002), which indicates that almost no export of particles occurs beyond this layer. This is consistent with the observation that for the southern and central Weddell Gyre the TCO_2 and O_2 values underneath the CIW range (i.e. $\theta < 0^\circ\text{C}$) are equal, whereas for the CIW this is clearly not the case (Fig. 2). Furthermore, Fischer *et al.* (2000) report an annual export fraction (fraction of primary production exported) at 1000 m as low as 0.01% from data of a sediment trap in the western Weddell Sea. Hence, our assumption appears to be firmly established.

For the central Weddell Gyre, the export production has been estimated using a chemical mass balance of the surface layer. Hoppema *et al.* (1999) found $19 \mu\text{mol C kg}^{-1} \text{ yr}^{-1}$, whereas Hoppema *et al.* (2002) report $16\text{--}17 \mu\text{mol C kg}^{-1} \text{ yr}^{-1}$ for different regions of the central Weddell Gyre and different years. Here we take $18 \mu\text{mol C kg}^{-1} \text{ yr}^{-1}$. With a winter mixed layer of about 100 m, the export production becomes $1.8 \pm 0.3 \text{ mol C m}^{-2} \text{ yr}^{-1}$ (relative error equal to that in Hoppema *et al.*, 2002). Note that here the winter mixed-layer should be taken because the export production in Hoppema *et al.* (1999, 2002) was determined as the annual nutrient deficit of the winter surface layer. As regards O_2 , the changes due to biological activity in CO_2 and O_2 are coupled through a Redfield ratio. We take $\Delta O_2 : \Delta \text{TCO}_2 = -170:117 = -1.45$ (Anderson and Sarmiento, 1994), as determined from changes in the deep global ocean. This value is in agreement with investigations on the composition of organic matter (Laws, 1991; Anderson, 1995; Fraga *et al.*, 1998). Thus, with respect to O_2 the export production becomes $2.6 \pm 0.5 \text{ mol } O_2 \text{ m}^{-2} \text{ yr}^{-1}$.

Using these values, the renewal time of the CIW layer was calculated for all regions and years for which we possess CIW inventories of TCO_2 enrichment and O_2 reduction. The results are included in Table 3. The results obtained from the O_2 depletion and TCO_2 enrichment inventories are consistent. The renewal time of the CIW is about three years, while the CIW of the western Weddell Sea may be somewhat older than the CIW at the prime meridian and in the far eastern Gyre. The calculated three years for CIW is relatively short for a water mass in the central part of the Weddell Gyre with weak currents (Fahrbach *et al.*, 1994). In contrast, the results suggest that the CIW is rapidly exchanged. Of note is that the renewal time of the CIW is similar to that of the surface layer of the Weddell Gyre (Gordon and Huber, 1990; Hoppema *et al.*, 1999).

b. Renewal rate of CIW

The mean transport (equivalent to renewal rate) of CIW can be estimated from the total volume of CIW present in the Weddell Gyre and its renewal time. Orsi *et al.* (1993) studied

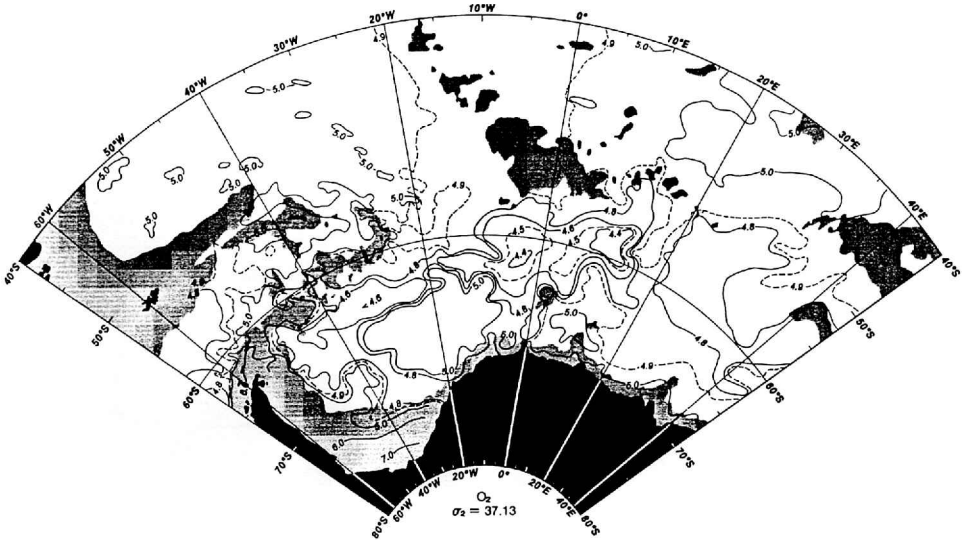


Figure 4. Dissolved oxygen in ml l^{-1} within the Central Intermediate Water, i.e. on the isopycnal $\sigma_0 = 27.883 \text{ kg m}^{-3}$ (or $\sigma_2 = 37.13 \text{ kg m}^{-3}$). Reprinted from Deep-Sea Res. I, 40, A. H. Orsi, W. D. Nowlin and T. Whitworth, On the circulation and stratification of the Weddell Gyre, 169–203, copyright(1993) with permission from Elsevier Science.

the regional distribution of CIW, in particular based on its O_2 concentration, the figure of which is reproduced here (Fig. 4). We took the surface area of CIW O_2 concentrations below 4.6 ml/l (units used by these authors), which is a reasonable limit for the CIW core (see Whitworth and Nowlin, 1987). The CIW core thus occupies $1.1 \cdot 10^6 \text{ km}^2$. With respect to the vertical extent of the CIW, the upper boundary is situated just below the pycnocline at about 200 m, whereas the 0°C isotherm (which is the defined lower boundary of CIW) occurs at about 1200 m. However, in the lower ranges the TCO_2 enrichment and O_2 reduction are very low or zero. Since the core of CIW with significant values ends at about 700–800 m depth, we took the vertical extent of CIW as 550 m. The total effective CIW volume is thus $6.1 \cdot 10^{14} \text{ m}^3$. With a mean CIW renewal time of three years the renewal rate (transport) of CIW becomes about 6.4 Sv ($10^6 \text{ m}^3 \text{ s}^{-1}$). This renewal rate is subject to an uncertainty, which is a combination of errors in the CIW volume and in the renewal time (Table 3). The former error can only be assessed. Tentatively we assess the overall error in the renewal rate to be of order 50%.

c. Significance of CIW

Rapid CIW renewal and its, accordingly, high transport are surprising because the CIW has been considered to be a water mass that is trapped in the central Weddell Gyre (Whitworth and Nowlin, 1987; Orsi *et al.*, 1999). These authors conjectured that the main CIW sink is the surface layer. We estimate the amount of CIW that is entrained into the surface layer is as follows.

Previously, Hoppema *et al.* (1999) have calculated that upwelling/entrainment in the interior Weddell Sea causes the annual substitution of a fraction of 0.345 of the surface layer by deep water (i.e. one third of the surface layer is annually exchanged). The residence time of the surface layer associated with this fraction (about three years) agrees well with the estimate of Gordon and Huber (1990). The upwelled subsurface water is essentially CIW. With a winter mixed layer of 100 m (see above) and a CIW surface area within the Weddell Gyre amounting to $1.1 \cdot 10^6 \text{ km}^2$ (see above), the volume of surface water that is substituted by CIW annually becomes $4.2 \cdot 10^{13} \text{ m}^3 \text{ yr}^{-1}$, which equals about 1.3 Sv.

Hence, only 20% (1.3 out of 6.4 Sv) of the CIW ends up in the surface layer. The remaining 80% or about 5 Sv of CIW must leave the central Weddell Gyre in a different way. There are different possibilities for CIW to escape the Weddell Gyre. Firstly, northward transport could occur at specific locations. A detailed distribution of the temperature maximum of the Weddell Gyre suggests that there may be outflow pathways of this sub-surface water near 15E and near 25W (Bagriantsev *et al.*, 1989). These routes should apply to the CIW as well. The distribution of O_2 in CIW as shown by Orsi *et al.* (1993) is not inconsistent with the above mentioned outflows (see Fig. 4). Secondly, CIW may be exported northward by means of widespread isopycnal mixing across the northern rim current of the Weddell Gyre. Whitworth and Nowlin (1987) observed an O_2 minimum north of the CIW region, at the northern rim, at similar density (but greater depth) as in the central gyre. As can be seen in Naveira Garabato *et al.* (2002), a remnant of CIW is found over the South Scotia Ridge, i.e. north of the rim current. Finally, Muench *et al.* (1990) suggest that the subsurface waters from the Weddell Sea end up in the deep Scotia Sea to the north. Additionally, Whitworth and Nowlin (1987: their p. 6475) notice that the nutrient maxima in the deep ACC north of the Weddell Gyre derive from the CIW, which is a strong indication indeed that northward CIW transport occurs.

The large CIW transport derived in the present study has important consequences for our view on the Weddell circulation. At the prime meridian the total transport of the gyre amounts to about 60 Sv (Beckmann *et al.*, 1999; Schröder and Fahrbach, 1999). Farther west across the Weddell embayment it is only half as large (Fahrbach *et al.*, 1994). Thus as Schröder and Fahrbach (1999) deduce, much of the westward flowing water north of Maud Rise near the prime meridian (39 Sv; their Fig. 13) feeds the Weddell interior. If we assume that about 25–40% of the full water column flow consists of CDW, the CDW source for the central Weddell Gyre is 10–15 Sv. Our calculations show that a substantial part of this is transformed into CIW, of which the major part leaves the gyre circulation. Although there is a large uncertainty in our CIW transport estimate, it is indeed probable that a major part of the inflowing CDW from the ACC feeds the CIW. The CIW is a major player within the Weddell circulation.

d. Methodological drawbacks and uncertainties

The CIW renewal time is calculated from the inventories of TCO_2 enrichment and O_2 depletion and the CO_2 supply/ O_2 fixation through the export production. The inventories,

in turn, are determined as the difference in concentrations between the source water CDW and its daughter CIW. For a CIW renewal time as exact as possible, the inventories of TCO_2 enrichment/ O_2 depletion should be accurate. This implies that the source water concentrations of TCO_2 and O_2 should originate from a location close to its entrance into the gyre circulation. For the calculation, we took the source water from the prime meridian but in fact, CDW enters the gyre farther east (Gouretski and Danilov, 1993). If CDW is biologically modified east of the prime meridian, the TCO_2 enrichment/ O_2 reduction would be larger, and hence CIW renewal time (as shown in Table 3) longer. However, both in the Southern Ocean Atlas (Gordon and Molinelli, 1986) and in the Hydrographic Atlas of the Southern Ocean (Olbers *et al.*, 1992), O_2 concentration in the O_2 minimum of the warm regime appears to be lower further east than on the prime meridian. The explanation for this is that between the eastern gyre and the prime meridian, mixing of CDW with waters above and below occurs (Usbeck, 1999). This leads to the situation of a low O_2 minimum upon CDW entrance and an increasing value of the minimum in western direction (at the prime meridian). Because of this intensive vertical mixing in the eastern gyre, it would be inappropriate to take warm regime water from that region to be the source of the CIW, for this would lead to an underestimation of the inventories. From the relatively low chlorophyll levels in the eastern gyre as compared to the west (Comiso *et al.*, 1993; Moore and Abbott, 2000), we assess that biological activity between the eastern gyre and the prime meridian is relatively small. Hence, the error due to uncertainty in the choice of the source water mass is probably relatively small, but most likely we slightly underestimate the renewal time of CIW.

Although between the eastern Weddell Gyre and the prime meridian, vertical mixing turns out to be a significant factor, west of the prime meridian only about 1.3 Sv (as computed above) of subsurface water is involved in vertical transport. This is a relatively small portion compared to the total CIW transport (renewal rate) out of the gyre.

It has been suggested by Bagriantsev *et al.* (1989) that there may be a second inflow of CDW into the Weddell Gyre near 20W. This inflow may be related to the existence of a double gyre structure for the Weddell Gyre (Orsi *et al.*, 1993; Beckmann *et al.*, 1999), where the western inflow would supply the western subgyre. For investigating this possibility, we assumed the source water for the western Weddell Sea to be the warm regime off Kapp Norvegia (see Fig. 1 for location). This reduces, relative to a supply of source water from the east, the inventories of TCO_2 enrichment/ O_2 reduction of the CIW for the western Weddell Sea and hence the CIW renewal time (Table 3). It is certainly possible that additional CDW inflow occurs near 20°W. The O_2 distribution within the CIW layer as shown by Orsi *et al.* (1993) shows a large patch of high oxygen in the southwestern Weddell Sea (Fig. 4), which could well derive from the source near 20W. If one would assume only one source in the east, the O_2 distribution along the westward flowing southern limb of the Weddell Gyre, with a lateral O_2 minimum, cannot be explained satisfactorily.

We estimate the impact of additional CDW inflow near 20W on the above calculated

CIW renewal rate as follows. The O_2 distribution in the CIW from Orsi *et al.* (1993) shows two bands of low- O_2 concentrations in the CIW (Fig. 4), which we here assume to correspond to the influence of the western and eastern gyre, respectively. The western band is much smaller with about $0.2 \cdot 10^6 \text{ km}^2$ than the eastern band ($0.9 \cdot 10^6 \text{ km}^2$). As above (Section 5c) the vertical extent of the CIW is taken as 550 m. With a renewal time of western CIW of two years (Table 3) this supports a CIW renewal rate of 1.7 Sv. For the eastern gyre the corresponding number is 5.3 Sv. The total CIW renewal rate/transport thus adds up to 7 Sv, which should be compared with the above calculated 6.4 Sv in Section 5c. Under this different scenario the CIW renewal rate is changed by less than 10%, which is within the overall uncertainty.

Another important assumption in the calculation of the CIW renewal time is that the CDW that entered the Weddell Gyre is only modified through biological activity. However, on its way through the gyre, the CDW and in particular its core may have been changed as a consequence of isopycnal and diapycnal mixing with the surrounding waters that are high in O_2 and low in TCO_2 . This would reduce TCO_2 and increase O_2 of the source water of the CIW, and thus lead to an underestimate of the CIW renewal time. In the following we estimate the sensitivity of the results to isopycnal and diapycnal mixing.

Diapycnal mixing with underlying Weddell Sea Deep Water (WSDW) should be considered. As suggested by one reviewer, we may refer to the work by Orsi *et al.* (1999), who modeled the upwelling speed at the top of Antarctic Bottom Water (which in the Weddell Sea includes the WSDW). For the Weddell Gyre these authors give a rate of around $5 \cdot 10^{-7} \text{ m s}^{-1}$, equivalent to about 15 m yr^{-1} . Over a time scale of three years (i.e. the CIW renewal time), and a CIW vertical extent of 1000 m, diapycnal mixing appears to be relatively insignificant. It should be mentioned, though, that the zero TCO_2 enrichment and O_2 depletion near the bottom of the CIW layer could be partly explained by the upward entrainment of WSDW.

Isopycnal mixing with adjacent water from the rim and vertical mixing with surface waters is likely to have impact. Whitworth *et al.* (1998) suggest that particularly the latter process causes the gradual reduction of the temperature maximum of the CDW, which appears comprehensible as during its course through the gyre a large portion of the CDW will not be in contact with the rim. We roughly assess the influence of vertical mixing on the CDW in the following way. Figure 5 shows potential temperature versus salinity diagrams for the prime meridian, in which the warm regime CDW is compared to its daughter CIW. It can be seen that in the lower temperature range the salinity of CDW and CIW is nearly equal. In the upper CIW temperature range ($0.4\text{--}0.7^\circ\text{C}$) the salinity of CIW is lower than that of the source water CDW. We perform a sensitivity analysis for cruises ANT XIII/4 (1996) and ANT XV/4 (1998). All data used appear in Table 4 and the procedure is as follows. For our assessment we assume that these changes in salinity are caused by mixing with overlying surface water. We distinguish two cases. The first case concerns the uppermost water of the CIW layer, which in Figure 5 are those points that lie farthest away (left) from the main, nearly linear relationships. This is the water that has

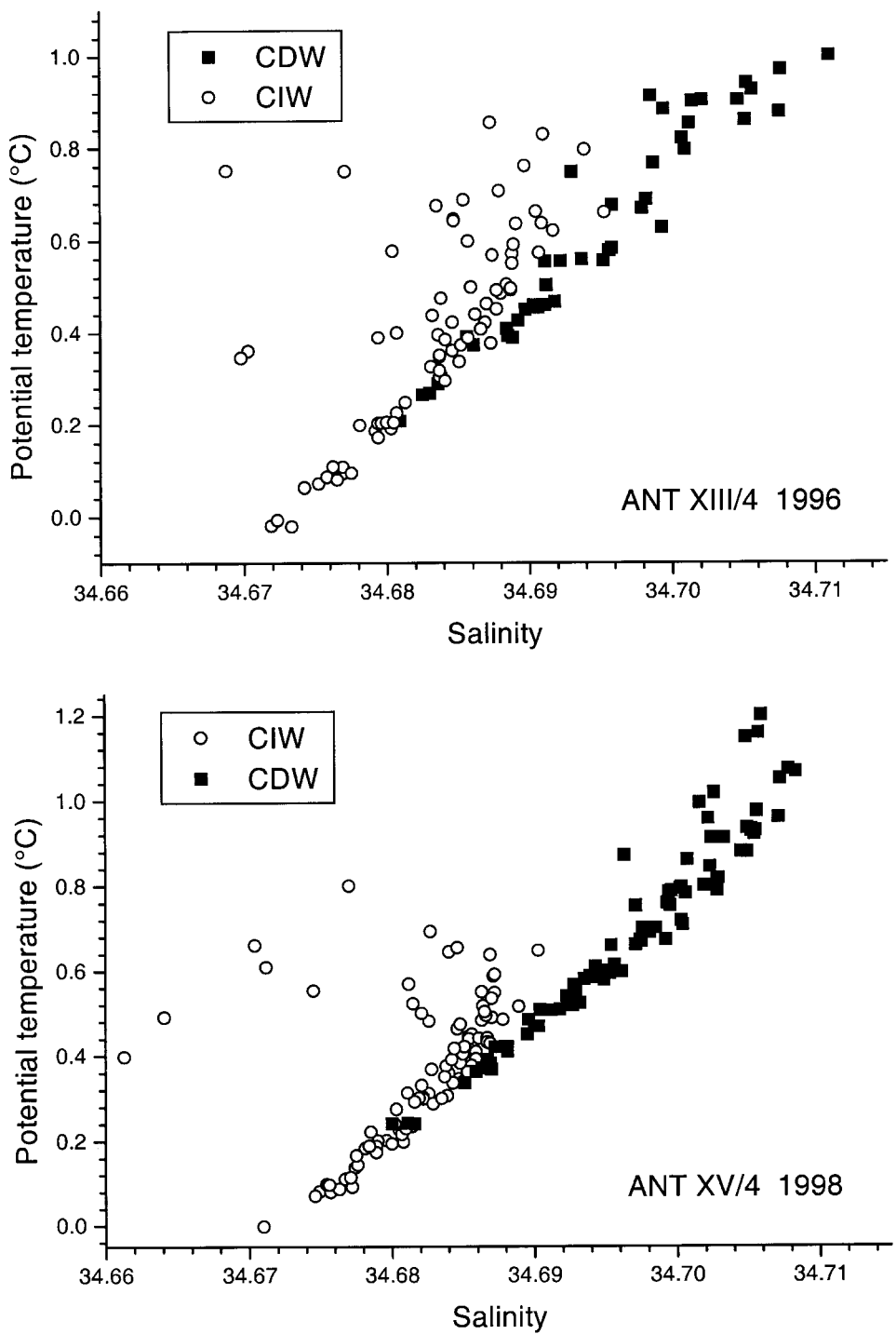


Figure 5. Salinity versus potential temperature diagrams at the prime meridian during cruises ANT XIII/4, 1996 (above) and ANT XV/4, 1998 (below).

Table 4. Data used in a sensitivity analysis on the influence of vertical mixing on the TCO₂ enrichment and the oxygen depletion of the CIW.

	1996 Temp. 0.4–0.5°C	1996 Temp. 0.5–0.7°C	1998 Temp. 0.4–0.6°C	1998 Temp. 0.6–0.7°C
S_{CDW}	34.69	34.695	34.69	34.695
S_{CIW}	34.685	34.685	34.685	34.68
F_{surf}	0.01	0.02	0.012	0.035
TCO ₂ (CDW) (· mol kg ⁻¹)	2261.5	2260.3	2264.5	2263.7
O ₂ (CDW) (· mol kg ⁻¹)	201.1	199.2	204.2	202.8
del-TCO ₂ (· mol kg ⁻¹)	0.7	1.3	0.8	2.2
del-O ₂ (· mol kg ⁻¹)	1.2	2.5	1.5	4.5
CIW vertical extent (m)	150	200	200–250	100
· TCO ₂ inventory (mol m ⁻²)	0.1	0.3	0.2	0.2
Total · TCO ₂ (mol m ⁻²), with % of total CIW TCO ₂ enrichment		0.4 (= 7%)		0.4 (= 11%)
· O ₂ inventory (mol m ⁻²)	0.2	0.5	0.4	0.4
Total · O ₂ (mol m ⁻²), with % of total CIW O ₂ depletion		0.7 (= 0%)		0.8 (= 13%)

Surface layer values used (concentrations in · mol kg⁻¹, not salinity): ANT X/4 (1992): S = 34.22; TCO₂ = 2201.5; O₂ = 326 (stations 579–606, i.e. prime meridian) ANT XIII/4 (1996): S = 34.20; TCO₂ = 2196; O₂ = 306 (stations 52–62, i.e. warm regime prime meridian) ANT XV/4 (1998): S = 34.30; TCO₂ = 2203; O₂ = 333 (stations 82–90; 96–98, i.e. warm regime prime meridian).

been influenced most by surface waters, as evidenced by its relatively low salinity. The second case treats the water near 0.4–0.5°C, which show only a small salinity difference between CDW and CIW. The temperature ranges chosen for the two cruises are specified in the header of Table 4. For each temperature range a typical salinity in the CDW (S_{CDW}) and CIW (S_{CIW}) is selected from Figure 5. Using a surface water salinity (Table 4), the fraction of surface water (F_{surf}) is simply calculated to bring the salinity from the CDW value to the CIW value. The surface water salinity is taken from autumn (cruises ANT XIII/4 and ANT XV/4) and winter (cruise ANT X/4) data on the prime meridian, because in these seasons most vertical mixing occurs. The fractions range from 1 to 3.5% (Table 4), where the highest fractions correspond to the uppermost CIW layer. Then the TCO₂ and O₂ contributions resulting from surface water (del-TCO₂ and del-O₂, respectively) were computed as follows:

$$(1 - F_{surf}) \cdot TCO_2(CDW) + F_{surf} \cdot TCO_2(surf) = TCO_2(CDW')$$

(1)

$$del-TCO_2 = TCO_2(CDW) - TCO_2(CDW')$$

(2)

An analogous set of equations exists for oxygen. TCO₂(CDW) and O₂(CDW) are obtained from the relationships in Table 1 at the appropriate temperatures. TCO₂(surf) and O₂(surf) are surface water concentrations for autumn and winter, like salinity above. del-TCO₂ and

del-O₂ are valid over a certain depth range within the CIW, which corresponds to the temperature range. The areal value of del-TCO₂ and del-O₂ is thus obtained by multiplying with the vertical extent of CIW. The final underestimation of the inventories of TCO₂ enrichment and O₂ depletion are <13% for the 1998 data and <10% for the 1996 data (Table 4). This corresponds to an underestimation of the CIW renewal time (see Table 3) of 0.3 years at most. Thus, as a final outcome of our assessment, diapycnal mixing of CDW with surface water does only have a minor impact on the results of the computation of CIW renewal time and renewal rate. It must be emphasized that these error estimates are exaggerated scenarios, where the likely underestimation will be smaller. In any case, in the light of the CIW transport estimate in Section 5c, where we took the CIW renewal time to be three years, an adjustment of the results is not necessary. Note that a slight increase of the renewal time would decrease the CIW transport estimate. Previously in this Section we assessed that the actual CIW transport may be somewhat higher due to processes occurring in the western Weddell Sea. These modifications partly compensate each other.

e. CIW and the biological pump

With regard to the biological pump, CIW is a crucial conduit for carrying CO₂ to the abyssal ocean basins. Briefly, CO₂ is fixed by primary producers (algae) in the surface layer of the central Weddell Gyre and moved to the underlying CIW against its own vertical gradient by virtue of the biological pump. The remineralized CO₂ is then by physical processes efficiently and comparatively rapidly transported to the deep oceans north of the Weddell Gyre, from where it circulates at abyssal depths in all oceans basins and is sequestered for many hundreds of years. This is the most effective physical-biological coupling for transferring CO₂ to the deep sea. In the temperate and tropical oceans the biological pump is almost solely dependent on particulate organic matter transfer to the deep sea. Clearly, only a very small percentage of the export production in these regions reaches the abyss because the major part is remineralized in the upper water column (e.g. Lampitt and Antia, 1997). In contrast, in the Weddell Gyre, some 80% of the export production may make it to the abyssal oceans through northward transport of CIW.

Sequestration of CO₂ in the Southern Ocean is often brought in connexion with bottom and deep water formation. However, this is a misapprehension. Bottom and deep waters are formed from CDW and a surface water component, the latter of which must have been generated from upwelled deep water somewhere around the Antarctic. In this process, CO₂ is emitted to the atmosphere because this deep water is highly supersaturated with CO₂ (Wanninkhof and Feely, 1998). Even if the CDW that participates in bottom water formation has collected some remineralized CO₂, the likely net effect of bottom water formation is a loss of CO₂ to the atmosphere as compared to its source water masses before these entered the Southern Ocean. In contrast, CIW formation only involves subsurface water masses, which keep their supersaturated CO₂ locked away from the atmosphere. It is important to appreciate, though, that bottom water formation does constitute a potential

conduit for sequestering anthropogenic CO_2 in the deep oceans because uptake of anthropogenic CO_2 is associated with ventilation. This uptake is superimposed on the natural process, which releases CO_2 to the atmosphere.

f. Renewal time versus ventilation age

It would be useful to compare the CIW renewal time with other estimates of the age of CIW, but unfortunately this is impossible. All existing methods that allow estimating the age of a water mass are based on ventilation of that water mass versus the surface ocean. Here ventilation means contact with the atmosphere. The CIW is a subsurface water mass which does not have direct contact with the atmosphere. Our method is thus unique and represents the only way of coming to an estimate of the renewal of subsurface water masses. Klatt *et al.* (2002) estimated the ventilation based age of water in the central Weddell Sea (corresponding with the lower part of the CIW) to be 19 years for a tracer-bearing part of only 8%. This is the least ventilated water mass in the Weddell Gyre indeed, which is clearly indicated by a CFC minimum (Schlosser *et al.*, 1991; Hoppema *et al.*, 2001). The ventilation overturning is estimated to be as long as 240 years (Klatt *et al.*, 2002). This is in accord with the view arising from our results for the CIW, which say that CIW is hardly ventilated and the water leaves the Weddell Gyre relatively rapidly.

6. Conclusions

Appropriate knowledge of biogeochemical parameters allows the calculation of physical properties of water masses. The conditions in the Weddell Gyre appear optimal for this, but also in other subpolar regions of the Antarctic Ocean such methods may find application.

Contrary to previous views, the endpoint for the CIW is not predominantly the surface layer (Whitworth and Nowlin, 1987), but rather it leaves the gyre to the north. Hence it influences the properties of the deep waters in the ACC, just like the deep and bottom waters locally produced in the Weddell Sea.

The remarkable coupling between biological (reservoir for export production) and physical (water mass transport) processes make CIW formation a highly efficient mechanism for the biological pump. The major part of exported production of the central Weddell Sea thus enters the abyssal oceans, whereas in other ocean provinces this is only a minor part. This renders the CIW an outstanding mediator for CO_2 sequestration. However, this does not hold for anthropogenic CO_2 sequestration, which depends on ventilation of nascent abyssal water masses. The CIW contribution to abyssal water masses may be one part of the explanation for the minor occurrence of anthropogenic CO_2 in deep and bottom waters flowing equatorward (Gruber, 1998).

Changes in CIW CO_2 inventory or transport may have an impact on atmospheric CO_2 levels. In glacial-interglacial issues which may be accompanied by changes in export production and/or in circulation, this may have contributed to observed changes.

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